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Facile Li/HMPA-Promoted Polymerization Method for the Synthesis of Soluble Poly(phenylenes)

by

James M. Tour and Eric B. Stephens
Department of Chemistry
University of South Carolina
Columbia, SC 29208

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A synthesis of poly(phenylene) is described by the treatment of 1-bromo-4-lithiobenzene with hexamethylphosphoramide (HMPA). The polymerization occurred nearly instantaneously even at -78°C. Conditions have been optimized using dioxane as a solvent and HMPA addition at 70-80°C to afford poly(phenylenes) that are predominantly *para*-linked. The polymers are soluble in THF, dichloromethane, and chloroform. Analysis of the initially formed polymers showed that there was a high bromide content (approximately one bromide for every three aryl rings). Debromination of the material was achieved by treatment with butyllithium and quenching with water. The M_w of the debrominated polymer was 3178 by SEC analysis. Functionalization of the polymer was demonstrated by the lithium-halogen exchange on the initially formed brominated polymer followed by quenching with carbon dioxide to afford the carboxylated polymer. The brominated and debrominated polymers were shown to be electroactive.

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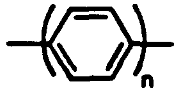
James M. Tour*,[1] and Eric B. Stephens
Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

REVISED

Abstract

A synthesis of poly(phenylene) is described by the treatment of 1-bromo-4-lithiobenzene with hexamethylphosphoramide (HMPA). The polymerization occurred nearly instantaneously even at -78°C. Conditions have been optimized using dioxane as a solvent and HMPA addition at 70-80°C to afford poly(phenylenes) that are predominantly *para*-linked. The polymers are soluble in THF, dichloromethane, and chloroform. Analysis of the initially formed polymers showed that there was a high bromide content (approximately one bromide for every three aryl rings). Debromination of the material was achieved by treatment with butyllithium and quenching with water. The M_w of the debrominated polymer was 3178 by SEC analysis. Functionalization of the polymer was demonstrated by the lithium-halogen exchange on the initially formed brominated polymer followed by quenching with carbon dioxide to afford the carboxylated polymer. The brominated and debrominated polymers were shown to be electroactive.

Poly(p-phenylene) (PPP) (1) has attracted much interest since it can act as an



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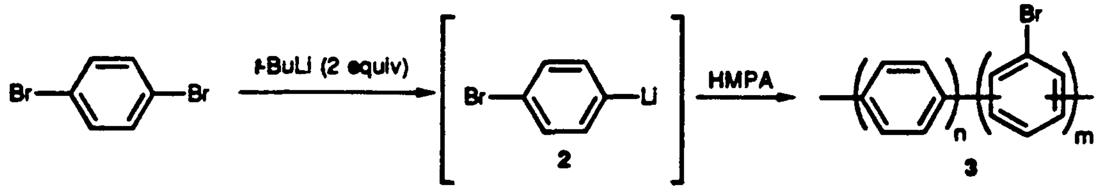
excellent organic conductor upon doping.[2] The conductivity of doped PPP has reached beyond the semiconducting and into the conducting region with values of 500 $\Omega^{-1}cm^{-1}$ being reported for the pressed pellets (films could not be formed due to the insolubility). There have been numerous syntheses of PPP; however, in nearly all cases, the materials are insoluble and intractable in organic solvents.[3-10] The most widely used methods for PPP formation involve the Kovacic and Yamamoto approaches that afford materials with degrees of polymerization of 10-15.[2] Thus these are oligomeric materials.

Here we report the nearly instantaneous polymerization of 1-bromo-4-lithiobenzene (2) by treatment with hexamethylphosphoramide (HMPA)[11] to afford poly(phenylene) which is predominantly *para*-linked. Some amount of *meta*-linkages causes the crystallinity to be destroyed rendering polymers that are soluble even with degrees of polymerization ~40. The ability to form soluble and tractable poly(phenylenes) which are predominantly *para*-linked could possibly allow new applications of this material for light weight rechargeable battery and electrochemical cell fabrications.[2,12]

Our initial approach involved the formation of (2) by the treatment of 1,4-dibromobenzene in ether at -78°C with two equivalents of *t*-butyllithium in pentane (slow addition). The first equivalent was for lithium-halogen exchange to form 2 and *t*-butyl bromide. The second equivalent of the *t*-butyllithium was necessary for the elimination of the *t*-butyl bromide to afford lithium bromide, isobutylene, and isobutane. This conveniently made all the by-products innocuous. (The intermediacy of 2 was confirmed in a separate experiment by the addition of chlorotrimethylsilane to form 1-bromo-4-(trimethylsilyl)benzene in nearly quantitative yield.) Compound 2 was then treated at the same temperature with HMPA (1 equivalent relative to the starting dibromide) which promoted the nearly instantaneous polymerization to poly(phenylene) with a high bromide content (3) (eq 1). Note that we have even quenched the reaction at -78°C by rapidly pouring



(1)

the mixture into water to confirm that the polymerization was indeed taking place at that temperature. This represents a new method of extremely facile, non-transition metal-catalyzed aryl-aryl polymerization.

Our optimal procedure[13] for forming poly(phenylene) with high concentrations of *para*-linked moieties was similar; however, the solvent used was dioxane, *t*-butyllithium was added at 0°C, and infusion of HMPA was done at 70-80°C.[14] This afforded polymer (3) with one bromide group for approximately every three aryl rings in 25-30% yield after one fractional precipitation from ether.[15] It is clear from the FTIR analysis that predominantly *para*-linked material is formed by the strong band at 808 cm^{-1} with weak bands at 882 and 790 cm^{-1} attributed to the *meta*-linkages.[16] A band at 1900 cm^{-1} was also attributed to the *para*-substituted units while the C-Br stretch was evident at 1074 cm^{-1}.[5] The polymer was soluble in THF, dichloromethane, and chloroform. The presence of phenylated polyphenylene can not be ruled out at this point.[9] Though powder X-ray diffraction (XRD) signals have been reported for Kovacic[2b] and Yamamoto PPP,[5] no diffraction pattern was observed for 3, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed a globular morphology pattern. Size exclusion chromatography (SEC) showed that 3 had a M_w = 2404 and M_w/M_n = 2.33 relative to polystyrene and oligo(*p*-phenylenes).[17] There was little, if any, aliphatic material present in the polymer by ^1H NMR.

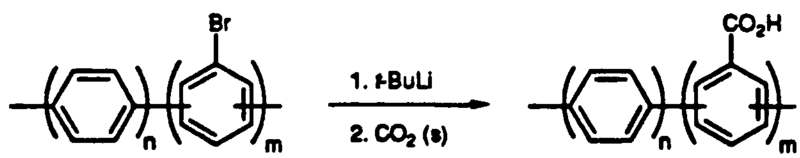
In order to accomplish debromination, 3 was dissolved in THF and cooled to -78°C. *t*-Butyllithium was added and the solution was stirred for 1 h at the same temperature before being quenched with water to afford the debrominated polymer 4. There was 0% bromide content by elemental analysis. Again, no aliphatic material was present in the sample. Remarkably, the M_w of our polymer increased from 2404 to 3178 (M_w/M_n = 2.80) upon debromination while the material remained soluble with degrees of polymerization >40. Some possible explanations could be that (1) the bromide content in 3 caused the polymer to be retained more tightly by the SEC columns (cross-linked polystyrene) and thus respond as a lower molecular weight material or (2) re-lithiation caused a further coupling of the chains. The solubility of the material suggests that there was little or no crosslinking of the chains. Again, no powder XRD signals were observable and SEM showed a globular morphology.

The reported CP/MAS/^{13}C NMR for PPP varies according to the method of preparation. Kovacic PPP shows resonances at δ 139, and 128 while commercial PPP has shifts at δ 143, 133, 130, 124.[18] For compound 4, the ^{13}C NMR (125 MHz, $CDCl_3$) chemical shifts obtained were at δ 140.66 (br), 128.80, 127.26. Further, the proton spin lattice relaxation times (T_1) of oligo(phenylenes) are known to decrease with increased chain lengths and ranges of 910 s for biphenyl to 0.48 s for PPP have been reported.[19] We found that compound 4 exhibited a T_1 range 0.9 - 1.4 s, consistent with high molecular weight material.

The UV data for oligo(phenylenes) have been reported. The value of λ_{max} for *p*-sexiphenyl and *m*-sexiphenyl are 318 and 248 nm, respectively.[20] Polymers 3 and 4 showed λ_{max} at 274 and 278 nm, respectively. Again, these values are indicative of mixtures of *para*- and *meta*-linked units.

We demonstrated that the polymers prepared by this Li/HMPA-promoted coupling are electroactive. A Pt-electrode was coated with films of both compounds 3 and 4. Anodic peak potentials (E_{pa}) for the oxidation were at 1.44 and 1.45 V, respectively.[21]

Additionally, we used the lithiated polymer to prepare functionalized derivatives. For example, 3 was lithiated as described above and quenched with dry ice to afford the carboxylated polymer 5 with one carboxylic acid moiety per three aryl units (eq 2).[22] The FTIR (KBr) spectrum was free of the C-Br stretch at 1074



3 5

(2)

cm^{-1} with the major stretch at 1686 cm^{-1} for the carbonyl moiety. The O-H stretch was weak presumable due to restricted hydrogen bonding in the solid. This procedure could have applications for the synthesis of functionalized polymers for self-doped conducting systems with fast electrochromic switching times and the fabrication of polymer-based batteries with high charge storage capacities.[23]

We do not have a clear understanding of the mechanism of the aryl couplings. The surprising aspect is that 3 unquestionably exhibits a predominance of *para*-linkages while much of the bromide content is retained. Migrations of lithium and bromide in bromo-lithio(heteroaromatics) are known under the base catalyzed halogen dance (BCHD) conditions.[24] The Taylor approach to PPP involving 1,4-dichloro-2-butene as a promoter for the polymerization of (4-bromo)phenylmagnesium bromide may involve similar electron transfer phenomena.[6] Additionally, the copolymerization of 2,5-dilithiothiophene with 2,5-dibromothiophene to afford poly(thiophene) has been reported.[25] However, as we described here, the addition of HMPA dramatically facilitates the aryl-aryl coupling process. A study of the scope and mechanism[26] of the polymerization as well as the detailed electrical and thermal analyses of the materials is in progress.

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(11) *Caution*: HMPA is a highly toxic cancer suspect agent. All manipulations with this material should be carried out in a well ventilated hood and rubber gloves should be worn.

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(13) The optimal procedure described provided the highest molecular weight material by SEC analysis with the greatest *para/meta*-containing ratio as determined by FTIR analysis. Using ether as the solvent, the M_w values for -78°C and 35°C HMPA additions were 1064 and 1739, respectively. Using THF as the solvent, the M_w values

for -78°C and 60°C HMPA additions were 668 and 1663, respectively. Using dioxane as the solvent with HMPA addition at 22°C, the M_w value was 1950.

(14) A reflux condenser is needed since a strong exothermic reaction ensues during the HMPA addition. The polymerization is complete immediately after the HMPA addition.

(15) Calculated elemental data for one Br per three aryl units: $C_{18}H_{11}Br$; C = 70.36, H = 3.58, Br = 26.06. Found: C = 68.94, H = 4.11, Br = 25.22.

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